

Title Transparent rubber modified styrene series resin composition

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Abstract

The present invention relates to a transparent rubber modified styrene series resin composition which comprises rubber particle disperse phase formed from rubber-like copolymer and copolymer continuous phase consisting of styrene series monomer, (methyl) acrylic ester series monomer, acrylonitrile series monomer and other monomer which can be copolymerized. By controlling the content of polystyrene block of rubber-like copolymer, ratio of rubber particles containing occlusion and content ratio of molecular weight being 3000-50000 in the continuous phase it can make the resin composite possess excellent resistance to chemicals and workability, at the same time it also can make its transparency and resistance to impact obtain equilibrium.

What is claimed is:

1. a transparent rubber modified styrene series resin composition, wherein: the resin composition comprises: rubber particle dispersive phase (A) formed by rubbery copolymer, and copolymers

continuous phase (B), wherein the rubbery copolymer contains: styrene monomer 10-50 weight %, and a diene monomer 90-50 w% block copolymer, above-mentioned rubber-like copolymer therein the content of polystyrene block accounts for rubber-like copolymer 5-35 weight %; while the copolymer continuous phase (B) is prepared from total amount of 100 weight parts styrene monomer 12-70 weight parts, (methyl) acrylic acid ester monomer 20-80 weight parts, acrylonitrile series monomer 1-20 weight parts, and other copolymerizable monomer 0-40 weight part, and copolymer continuous phase (B) therein molecular weight 3, 000-50, 000 accounts for all copolymer continuous phase (B) 15-50 wt%.

2. transparent rubber modified styrene series resin composition according to claim 1, which is characterized in that: rubber particle dispersive phase (A) therein the number of the rubber particle containing four or more occlusion structure accounts for all the rubber particles numbers of 2-20%.

3. transparent rubber modified styrene series resin composition according to claim 1, which is characterized in that: the number of rubber particle dispersive phase (A) without occlusion structure rubber particle accounts for all the rubber particle number 20-80%.

4. transparent rubber modified styrene series resin composition according to claim 1, which is characterized in that: rubber-like copolymer is block copolymer with gradually increasing components.

5. transparent rubber modified styrene series resin composition according to claim 1, which is characterized in that: the rubber-like copolymer therein polystyrene block content is 10-25 w%.

6. transparent rubber modified styrene series resin composition according to claim 1, which is characterized in that: the rubber-like copolymer therein polystyrene block content is 14-22 w%.

Description

Transparent rubber modified styrene series resin composition

The invention relates to a transparent rubber modified styrene series resin composition, specifically relates to a comprises copolymer continuous phase, and formed of rubbery copolymer rubber particles discontinuous phase, and has preferred chemistry pharmaceutical product resistance, processability, good transparency and impact resistance physical property balanceable resin composition.

Rubber modified styrene resin is a material with good intensity and processing to ability, since the kind of resin has above-described advantages, hence widely is used in foodstuffs container, package material household products, home appliances product, and OA machine casing, but since the common rubber modified styrene resin does not transparent, thereby, cannot used on transparent articles shaping. In order to satisfy resin intensity and good transparency, and resin physical property get balance, in existing art may be styrene series resin and styrene-butadiene block polymerization material kneading, but this method cannot sufficient to increase resin intensity, on used is not satisfactory. While the Japan special kaiping the first 4-180907 number invention patent applications table, which is to provide an in the presence of styrene-butadiene block polymerization broth, and styrene and methyl methacrylate copolymerization method, the method although can improve resin transparency and intensity, but cannot satisfy the processing to sexual requirements.

While the Japan special kaiping the first 8-239532 number invention patent applications table is in the provides a: styrene-butadiene rubber, and inflectional rate similar styrene-methyl methacrylate formed copolymerization of composition. Said composition rubber having an average particle diameter of 0.1-2 μ m, and 1, 2-vinyl rate is 1-13.8 weight %, particle diameter distribution index is 2-5, the composition despite can improve resin transparency and impact resistance, but cannot improve resin chemistry pharmaceutical product resistance.

The inventors after be bent on research discovery, by the benzene ethylene monomer, (methyl) acrylic acid ester-series monomer and acrylonitrile monomers comprized copolymer continuous phase, mating containing a rubbery copolymer rubber particle disperse phase formed, and the mating the continuous phase and a dispersed phase specific constructed and conditions, make the can make rubber modified styrene series resin composition has preferred transparency and chemistry pharmaceutical product resistance, simultaneously resin each physical property between also can obtain balance.

The present invention relates to provide a with good chemistry pharmaceutical product resistance, processability, and transparency and resistance to impact and other physical property balance good transparent rubber modified styrene series resin composition.

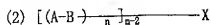
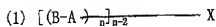
The inventive transparent rubber modified styrene series resin composition is comprises: rubber-like copolymer formed of a ground rubber particle dispersive phase (A), and copolymer

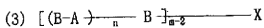
continuous phase (B); wherein, the rubbery copolymer is containing benzene ethylene monomer 10-50 weight %, and a diene monomer 90-50 w% block copolymer, above-mentioned rubber-like copolymer therein the content of polystyrene block accounts for rubber-like copolymer 5-35 weight %, while the copolymer continuous phase (B) is prepared from total amount of 100 weight parts styrene monomer 12-70 weight parts, (methyl) acrylic acid ester monomer 20-80 weight part, acrylonitrile series monomer 1-20 weight parts, and other copolymerizable monomer 0-40 weight part manufactured, and copolymer continuous phase (B) therein molecular weight 3, 000-50, 000 person based on all the copolymer continuous phase (B) 15-50 weight %; further regard, the rubber particle dispersive phase (A) therein rubber containing four or more than occlusion structure particle number accounts for all the rubber particles numbers of 2-20%, while in rubber particle dispersive phase (A) without occlusion structure rubber particle number accounts for all the rubber particle number 20-80%;

According to the above resin, can obtain the invention required has preferred chemistry pharmaceutical product resistance and processability, simultaneously can obtain good transparency and resistance to impact intensity balance physical property resin composition. The invention used rubber-like copolymer is in the presence of organic solvent, use of organo lithium compounds as initiator, and styrene monomer, diene monomer, appropriate amount of solvent perform anionic polymerization to block copolymer, above copolymers wood nylon (Moony) viscosity (ML.1+4) is 20-80, 25 \square 5 w% benzene ethylene monomer solution viscosity is 3-60 cps, while diene unit therein 1, 2-vinyl structure for accounts for over 8 wt%, the content of polystyrene block accounts for rubber-like copolymer 5-35 weight %, of the above-mentioned rubber-like copolymer structure can be: all homopolymer block structure, part of disordering discharge block structure, taper-block structure, linear structure and splice structure etc. representative structure with:

1, linear block polymerization material: (1) (A-B) $_n$ in the above formula, A therefore styrene is main component polymer block, B therefore the diene is main component polymer block, A block with the B block margin not a certain require explicit differentiated, $n=1$ or integer over 1.

2, splice type block copolymer:





In the above formula, A, B with first item show, X is coupler residue (for example: silicon tetrachloride, tin tetrachloride), or polyfunctional organic lithium compound residue, n and m is an integer from 1-10. 3, the above first items and a second nuchal arbitrarily formal mixture. In addition, set of component increasing block structure can be styrene increasing block structure, or is butadiene increasing block structure, above increasing block structure specifically instance with:

D-D/S-S	(S-D/S) n-S
D-S-D/S-S	D/S-(S-D/S) n
D-S-D/S-S-D	X-[(S-D/S) n]m+1
S-D-D/S-S	X-[(D/S-S) n]m+1
D/S-S-D-S	X-[(S-D/S) n-S]m+1
S-D/S-S	X-[(D/S-S) n-D/S]m+1
(S-D/S) n	D-D/S-S-S-D/S-D

Wherein, S is polystyrene series block, D is polydiene block, D/S is styrene series or diene component content of increasing styrene-diene copolymer block, X is polyfunctional initiator group or polyfunctional couplers for base, m, n is an integer from 1-10, above specifically instances take D-D/S-S or D-S-D/S-S, D-D/S-S-S-D/S-D as preferred. With respect to the invention, to increasing block structure better suited.

The invention of rubber-like copolymer therein polystyrene block content is 5-35 weight %, preferred is 10-25 weight %, and even more preferably 14-22 weight %, when the content of polystyrene block of less than 5 w%, the resin transparency in difference, the opposite, the content when is greater than 35 w%, will be resulting in resin impact intensity fall, cannot to achieve the invention required transparency is balanced with impact intensity physical property purposes. In addition, the invention rubber therein 1, 2-vinyl structure content in over 8 w%, and take over 14 w% as preferred, when a 1, 2-vinyl content high when 14 w%, the resin transparency and impact resistance therebetween physical property balance preferred; the above styrene series monomer can be: styrene, α -methyl benzene with ethylene, p-methyl benzene ethylene, between-methyl benzene with ethylene, ortho-methyl benzene with ethylene, ethyl benzene ethylene, 2, 4-dimethyl benzene ethylene, p-third butyl benzene ethylene, α -methyl-p-methyl benzene ethylene,

bromine-styrene, dibromo-benzene ethylene, 2, 4, 6-tribromostyrene etc. above benzene ethylene monomer can be employed separately or thousands of kind of used in combination.

The inventive diene monomer is selected from: 1, 3-butadiene, 2-methyl-1, 3-butadiene, 2-methyl-1, 3-isoprene, 2, 3-double-methyl-1, 3-butadiene, 1, 3-isoprene, 1, 3-hexadiene etc. above compounds can be employed separately one or more than two kinds of mixing wherein in turn take 1, 3-butadiene or 1, 3-isoprene as preferred. The invention of rubber-like copolymer used organo lithium compound catalyst is molecule compound containing more than one of lithium atoms, which can select from: ethyl lithium, positive-pentyl lithium, isopropyl lithium, positive-butyllithium, secondary butyllithium, hexyl lithium, cyclohexyl lithium, phenyl lithium, benzene methyllithium, naphthyl lithium, third-butyllithium, three methylene bis lithium, tetramethylene dilithium, butadiene double lithium and isopentadiene as raw material dilithium such as one or more than two kinds of used in mixtures. The invention of rubber-like copolymer when aggregate aggregate velocity, 1, 2-vinyl content, and a diene monomer and benzene ethylene monomer reactivity ratios and disordering discharge state, capable of by polarity compound or random agent to adjust, the above polarity compound or disordering discharge agent is selected from the group consisting of: ethers, amines (amine), sulfide amine, alkylbenzenes, sulfon acids, alkyl oxide potassium or sodium salt.

The inventive transparency rubber modified styrene series resin composition, its rubber-like copolymer content is 1-40 weight %, when the content of less than 1 w%, the resin impact intensity decreases, exceeding 40 weight %, resin transparency and processing to form decreases. In addition, the inventive copolymer continuous phase (B) is prepared from 12-70 weight part styrene series monomers, 20-80 weight parts (methyl) acrylic acid ester-series monomers, 1-20 weight parts of acrylonitrile monomer, and 0-40 weight part other copolymerizable monomer manufactured, based on chemistry pharmaceutical product resistance, rigidity and transparency requirements, the acrylonitrile-series monomer content of take 2-12 weight part as is preferred, more preferably 2-10 weight part wherein styrene monomer specifically instance as detailed in the above a rubbery copolymer styrene monomer, herein not be repeatedly enumerated show.

While the above (methyl) acrylic acid ester-series monomer comprises: methacrylates and acrylic acid esters wherein methacrylates may for example: methyl methacrylate, methacrylic acid ethyl ester, butyl methacrylate etc. and acrylic acid esters for example: methyl acrylate, acrylic acid

ethyl ester, n-butyl acrylate, acrylic acid 2-methyl amyl acrylate, acrylic acid 2-ethyl amyl acrylate, acrylic acid octyl esters and the like wherein and take methyl methacrylate and acrylic acid methyl ester as preferred. The inventive acrylonitrile series monomer can be: acrylonitrile, α -methyl acrylonitrile by etc. the content of 1-20 weight parts, if acrylonitrile series monomer content of less than 1 weight part, resin chemistry pharmaceutical product resistance and rigidity, when content higher than 20 weight part, resin transparency, hue and processability of becomes worse.

Copolymers of the invention continuous phase (B) copolymerizable monomer 0-40 weight parts, its monomer types and not particularly restricted, depending on needs to be adjusted each copolymerization monomer content of proportional adjustments are inflectional rate, the last resin composition achieved transparent as necessary, above copolymerizable monomer specifically examples of: itaconic acid, maleic acid, fumaric acid, crotonic acid, lauric acid such as does not fatty acids; N-methyl maleinoyloxy imine, N-ethyl maleinoyloxy imine, N-butyl maleinoyloxy imine, N-octyl maleinoyloxy imine, N-isopropyl maleinoyloxy imine, N-phenyl maleinoyloxy imine, N-the p-bromo-phenyl maleinoyloxy imine, N-ortho-chlorine-phenyl maleinoyloxy imine, N-cyclohexane base of maleic acid imine and others maleic acid imines; cis-butylene diacid anhydride, methylene succinic anhydride, citraconic anhydride does not saturated carboxylic acid anhydride; allyl group amine, (methyl) acrylic acid amidocyanogen ethyl ester, (methyl) acrylic acid amidocyanogen propyl ester containing amidocyanogen does not saturated compounds; acrylamide, N-methylacrylamide and other acrylamide series of compounds.

The inventive resin composition, the copolymer continuous phase (B) therein molecular weight 3, 000-50, 000 person based on all the copolymer continuous phase (B) 15-50 weight %, preferred is 20-45 weight %, and even more preferably 25-40 weight %, when the molecular weight 3, 000-50, 000's content of less than 15 w%, resin processability of becomes worse, when in compliance with this range content higher than 50 w%, the resin impact intensity becomes worse, chemistry pharmaceutical product resistance also becomes difference; that is to say, only in compliance with above range, resin composition impact resistance preferred, simultaneously also has preferred processing to ability and chemistry pharmaceutical product resistance. The inventive copolymer continuous phase (B) polymer structure can be linear or bifurcation shape, wherein branch shape copolymer continuous phase (B) can obtain preferable impact intensity and processability of (fluidity) the physical property balance; above splice copolymer continuous phase (B) can be

made by implemented in a manner, for example: aggregate adopted or addition of containing polyfunctional does not saturated group-containing monomer, polyfunctional initiator, polyfunctional chain transfer agent one or more and used to accomplish.

In addition, the inventive rubber particle dispersive phase (A) therein rubber containing four or more occlusion structure of particle number accounts for all the rubber particles 2-20%, preferred is 3-15%, and even more preferably 3-10%; while in dispersed phase (A) without occlusion structure rubber particle number accounts for all the rubber particle number 20-80%, preferred is 30-75%, and even more preferably 40-70%, when the rubber particle dispersive phase (A) therein rubber containing four or more occlusion structure particle and proportions in number, and without an occlusion structure rubber particle proportion of the number of when the above within the set range, and can make the resin transparency and impact resistance get balance.

The invention so-called occlusion structure, it is meant that coated inside rubber particles of granular styrene series-(methyl) acrylic acid ester-series-of acrylonitrile copolymer, and therein bag particle diameter of whisker in 0.05 μm or from 0.05 μm above the starting can conform to the inventive included particles defined; disperse phase without occlusion rubber particles is rubber particle totally without occlusion or encapsulating particle diameter of less than 0.05 μm .

The inventive resin composition according to under various conditions matched, for example: aggregate state component adjustment, additive, devolatilizer, extrusion into adjustment, fog density (Haze) can accomplish not more than 11.0 degree.

The inventive resin composition copolymer continuous phase (B) a weight average molecular weight is not specifically limited, generally is 50, 000-300, 000, preferred is 60, 000-200, 000, more preferably 70, 000-150, 000, when a weight average molecular weight of less than 50, 000, resin composition impact resistant difference in intensity, whereas when a weight average molecular weight than the 300, 000, resin composition fluidity can be fall, processability poor and transparency is poor. In addition, the invention resin composition rubber particles weight average particle diameter does not particularly limited, generally in the 0.1-2.0 μm , preferred is of 0.1-1.5 μm , and even more preferably 0.2-1.0 μm , when rubber particles weight average particle diameter is less than 0.1 μm , resin composition impact intensity fall, if a weight average particle diameter is greater than 2.0 μm , then resin composition transparency is poor. Above rubber particles weight average particle diameter to permeate electron microscope ultra-thin slicing

method the illuminated to obtain a photograph, the photographs least 300 particles above, and the following formula determining weight average particle diameter.

$$\text{重量平均粒径} = \frac{\sum n_i D_i^4}{\sum n_i D_i^3}$$

wherein 重量平均粒径- differential molecular weight distribution

In the above formula n_i that particles having particle diameters of D_i rubber particles the number. Resins of the invention composition therein does not dissolve content and is not particularly restricted, is generally 2-40 weight %, preferred is 8-35 weight %, and even more preferably 12-30 weight %, when not soluble component content is less than 2 w%, resin composition impact intensity deficiency, and when not soluble parts of content is greater than 40 w%, resin composition fluidity of a variance, processing to ability and transparency is poor. In addition, the inventive resin composition therein swelling index and is not particularly restricted, generally in 2-25, preferred is 3-20, more preferably 5-15, when the invention-the resin composition swelling index of not in the range of 2-25, its physical property (impact intensity) and transparency cannot balance.

The above resin composition do not soluble component content of w% or swelling index measurement mode, have 1g resin composition dissolved in 1:1 toluene and acetone mixed solvent, and at 25 °C, 24 hr dissolves, then to centrifuge (15000 rpm, 20 minutes) separating, and then taking it that the underlying layer liquid to obtain the expanded does not dissolve weight, and will not soluble parts to 80 °C vacuum dry 12 hrs, to obtain does not dissolve weight, and then the following formula work out does not dissolve parts of content (weight %).

$$\text{不溶份的含量(重量\%)} = \frac{\text{不溶份的重量}}{\text{树脂组成物的重量}} \times 100\%$$

wherein 不溶份的含量(重量\%)-insoluble copies content(wt%); 不溶份的重量-insoluble copies weight; 树脂组成物的重量-resin composition weight

And the inventive swelling index therefore the following formula:

$$\text{膨润指数} = \frac{\text{膨润后不溶份的重量}}{\text{乾燥后的不溶份重量}}$$

wherein 膨润指数-swelling index; 膨润后不溶份的重量-insoluble copies weight after swelling;

干燥后的不溶份重量- insoluble copies weight after drying

The inventive rubber modified styrene series resin composition manufacture method, which is in the presence of rubber-like copolymer, and styrene monomer, (methyl) acrylic acid series monomer, acrylonitrile series monomer and if necessary addition of other copolymerizable monomer perform batch or continuous block-shaped or solution ingrafting polymerization reaction. Take continuous solution aggregate as an example, firstly adding the above rubber-like copolymer and monomer into proper solvent of raw materials a mixed solution, the above raw materials mixed solution can be carried out in conventional has high shear stress, high shaking down speed dissolves slot dissolves, the dissolves slot can make with: has ribbon-shaped the helical stirring vane, helical propeller stirring vane, or other can generate high shear stress stirring vane etc. under enough time, and can so as to above-mentioned rubber-like copolymer totally dissolves into rubber solutions state, to facilitate pump delivering to the reactor operation performing; the above raw materials solutions or monomer solution respectively continuous is fed into first reactor and/or second reactor, and/or its subsequent reactor, matched with required performing at first and/or second and/or thereof with subsequent reactor addition of chain transfer agent, initiator ingrafting polymerization reaction.

Reactor described above can be a continuous floatation type reactor (CSTR), or plug flow reactor (Plug flow reactor), or a static mixing well-formed (static reactor) reactor same or different kinds of combined; reaction temperature is controlled at 70-230 °C, final monomer conversion rate can be up to 30-95%, but take 50-90% as preferred.

The invention transparent rubber modified styrene resin aggregate mode, preferred is first reactor adopting continuous floatation type reactor (CSTR), and then followed by a second and/or subsequent reactor, the above subsequent reactor can be a continuous floatation type reactor, plug flow reactor or a static mixing well-formed reactor etc.

Generally the first reactor monomer conversion rate between about 1-30 weight %, preferred is 2-25 weight %, and even more preferably 3-22 w%. While the above the first reactor monomer conversion rate selected, is according to used rubbery copolymer of content type, viscosity of different to regulate, that is try to make rubber adverse rotary phenomenon does not in the first reactor generate, while in the subsequent reactor (such as a second or third reactors) can not be produced adverse rotate, thus, can obtain good physical property.

The invention transparent rubber modified styrene resin when aggregate, available solvent type with: of aromatic hydrocarbon, ketones, esters wherein the best of aromatic hydrocarbon for example: toluene, ethylbenzene and xylenes, while the ketones and most preferably butanone, esters take acetic acid ethyl ester as perfect; in addition, the invention also can use positive-ethane, cyclohexane, positive-heptane and the like fatty hydrocarbon as solvent part.

The invention transparent rubber modified styrene resin in manufacture, available initiator which adding additional amount is relative to 100 weight parts monomer 0-2 weight parts, preferred 0.001-0.7 weight part, specifically instance with: benzoyl peroxide, dicumylperoxide, di benzoyl superoxide, t-butyl peroxide, t-butyl hydroxy peroxide, cumene hydroperoxide, t-butyl peroxybenzoate, di-2-ethylhexyl peroxy dicarbonate, tert-butyl peroxy isopropyl carbonate, referred to BPIC, cyclohexanone peroxide, 2, 2'-azo-bis-isobutyronitrile, 1, 1'-azo-bis-1-cyclohexane carbonitrile, 2, 2'-azo-bis-2-methylbutyronitrile, azo-bis-isobutyronitrile, 1, 1-di-t-butyl peroxy cyclohexane, referred to TX-22, 1, 1-di-t-butylperoxy-3, 3, 5-trimethylcyclohexane, referred to TX-29A, 2, 5-dimethyl-2, 5-bis-(2-ethylhexanoxo peroxy) hexane, 4-(t-butyl peroxy carbonyl)-3-hexyl-6-[7-(t-butyl peroxy carbonyl) heptyl]cyclohexane, di-t-butyl-diperoxyazelaate, 2, 5-dimethyl-2, 5-bis-(benzoyl peroxy) hexane, di-t-butyl peroxy-hexahydro-terephthalate, referred to BPHTP, 2, 2-bis-(4, 4-di-t-butyl peroxy) cyclohexanyl propane etc.

The invention transparent rubber modified styrene resin in manufacture, can make with chain transfer agent addition of additional amount is relative to 100 weight part monomer 0-2 weight parts, preferred is 0.01-0.7 weight part, specifically instance with:

- 1) mercaptan: methyl mercaptan, positive-butyl mercaptan, cyclohexyl mercaptan, normal-dodecyl mercaptan, stearyl mercaptan, t-dodecylmercaptan, referred to TDM, positive-propyl mercaptan, normal-octyl mercaptan, third-octyl mercaptan, third-nonyl thiol etc.
- 2) alkane amine: monoethyl amines, bisethylamine, triethyl amine, single isopropyl amine, bismonopropyl amine, monobutyl amine, di-n-butyl amine, tri-n-butyl amine etc.
- 3) pentaerythritol tetrakis(3-mercaptopropionate), pentaerythritol tetrakis(2-mercaptoethanate), pentaerythritol tetrakis(4-mercaptopropanate), pentaerythritol tetrakis(5-mercaptopentenate), pentaerythritol tetrakis(6-mercaptohexanate), trimethylolpropane tris(2-mercapto ethanate), trimethylolpropanetris(3-mercapto propionate), referred to TMPT, trimethylolpropane

tris(4-mercapto butanate), trimethylolpropane tris(5-mercapto pentanate), trimethylol-propane tris(6-mercapto hexanate) etc.

Other for example: pentaphenylethane, α -methyl styrene dimer, terpinolene. The above polyfunctional does not saturated group-containing monomer addition additional amount relative to 100 weight parts monomer 0-1 weight parts, preferred is 0.005-0.6 weight parts, its specifically for example:

- 1) di vinyl benzene, 1, 2, 4-tri vinylbenzene, 1, 3, 5-tri vinyl benzene and other di ethylene.
- 2) ethylene glycol dimethacrylate, di ethylene glycol dimethacrylate, triethylene glycol dimethacrylate, polyethyleneglycol dimethacrylate, 1, 3-propylene glycoldimethacrylate, 1, 4-butylene glycoldimethacrylate, 1, 6-hexanene glycoldimethacrylate, neo pentyl glycol dimethacrylate, referred to PGDMA, dipropylene glycol dimethacrylate, polypropylene glycol dimethacrylate, 2, 2-bis-(4-methacryloxy diethoxy phenyl) propane and other di acrylic acid methyl ester.
- 3) trimethylol propane trimethacrylate, triethylol ethane trimethacrylate or the like three acrylic acid methyl ester.
- 4) ethylene glycol diacrylate, diethylene glycol diacrylate, tri ethylene glycol diacrylate, polyethylene glycol diacrylate, 1, 3-di-propylene glycol diacrylate, 1, 4-di-butylene glycol diacrylate, 1, 6-hexylene glycol diacrylate, neopentyl glycoldiacrylate, referred to PGDA, di propylene glycoldiacrylate, polypropylene glycol diacrylate, 2, 2-bis(4-acryloxy propoxy phenyl) propane, 2, 2-bis(4-acryloxy di ethoxyphenyl) propane or the like di acrylic acid esters.
- 5) trimethylol propane triacrylate, triethylol ethane triacrylate such as a triacrylate of categories.
- 6) tetramethylol methane tetraacrylate or the like four acrylic acid esters.

The above polymerization, then from reactor taking out removing volatile device, remove unreacted monomers, solvent low-volatile portion, via a polymer collection, then it can obtain the invention transparent rubber modified styrene series resin composition.

Above removing volatile device can be: single axle or dual-axis attached with devolatilizer mouth extruder, and can be according to the requirements in extruder is added devolatilizer auxiliary agent, such as: water, cyclohexane, carbon dioxide etc. While the extruder can also according to the requirements provided with kneading and mixing sector (kneading zone), push sector etc. screw rotation speed is 120-350 rpm. In addition, also can use attached with vacuumizing

equipment devolatilizer slot, the above devolatilizer groove can be 1 or several connected in series, temperature is controlled at 180-350 °C, preferred is 200-320 °C, more preferably 220-300 °C, while the devolatilizer groove vacuum degree is controlled below 300 Torr, preferred below 200 Torr, more preferably not more than 100 Torr; other devolatilizer device such as films vaporizer (thin film) can also adopt.

Via the above removing volatile device treatment, and can make resin therein residue monomer, solvents, 2 amount of bodies, three amount of body volatile component decrease to not more than 1 w%, preferred is not more than 0.8 w%, more preferably not more than 0.5 w%.

In the range of not remarkably loss of the invention resin composition effect, can prepare other components, these other components for example: inking agent, filling agent, fire retarding agent, hard to burn auxiliary agent (antimony trioxide such as), optical stabilizer, thermal stabilizer, plasticizer, lubricating agent, parting agent, tack-producing agent, electrically-charged preventing agent, oxidation preventing agent, conductive agents such as additives; the above additives may for example: mineral oil, for example: stearic acid butyl ester ester-based plasticizer, polyester plasticizer, for example polydimethyl siloxanes organopolysiloxanes, high level fatty acids and their metal salts, hindered amine antioxidants, fiber glass etc. It can be employed separately or as mixtures. Above component according to the requirements can be after polymerization stage or reaction is completed adding and mixing.

The above ester-based plasticizer or mineral oil the usage amount (based on resin composition) generally 0-5 weight %, preferred in the 0.05-2 weight %, and organopolysiloxanes the usage amount in general 0-0.5 weight %, preferred over an 0.002-0.2 w%.

In addition, in not remarkably loss of the invention resin composition transparency of case, be further formulated other resin, and can add other resin such as: styrene series-(methyl) acrylic acid ester-series-of acrylonitrile copolymer, styrene series-(methyl) acrylic acid ester-series copolymer, styrene-(methyl) acrylic acid ester-series-acrylonitrile series-maleic imine copolymer, benzene ethylene-(methyl) acrylic acid ester-series-maleic imine copolymer, (methyl) acrylic acid ester-series-maleic imine copolymer, or via a diene rubber upgrading (or ingrafting upgrading of) the above copolymer.

The above resin usage amount is relative to transparent rubber modified styrene series resin composition 100 weight parts 0-200 weight parts, thereof can adjust or to increase resin

composition heat resistance, rigidity and flow processability.

The inventive transparent rubber phenylethylene resin composition use and no particular limitation is imposed on, which can suitable for ejecting shaping, compression shaped various kinds of molded articles, extrusion moulding, blow delay molding, thermoforming, vacuum forming and hollow molding prepared final product, for example partition wall board, thin film molded article etc. can be according to formula blending to achieve high fluidity, high heat resistance such as demand.

The above other components or resins adding and mixing the capable of via cloth pulling the's plastic behavior instrument, Mylabris primary vertical kneading machine, kneading and-mixing machine, roll extrusion machine, a shafts or biaxial extruder or the like mixing in general kneading machine mixed. kneading so as to obtain the invented product. Usually by these extruder mixing. kneading, then then prepare extrusion extrudate was added to cool, granulating, above kneading is generally at 160-280 ° to perform, while the take 180-250 ° temperature as preferred, and each blending components. kneading and no order particularly limited.

[Physical Property Test]

- . processability (fluidity, referred to MI): according to ASTM D-1238 standard flow coefficient. for determining resin under 200 ° × 5kg.
- . chemistry pharmaceutical product resistance (oil resistance): emit resin molded 23 cm long test piece, and bend test piece is fixed on bow tester to form bow shape, test sheet surface coating olive oil placing at ambient temperature, after 6 hr observe the exterior appearance.
 - : representing test piece exterior appearance did not change.
 - : representing test piece exterior appearance slightly cracks hachure.
 - ×: representing test piece exterior appearance cracking a serious problem.
- . impact resistance (IZOD): depending on ASTM D-256 measuring Ehrlich impact intensity (23 ° attached gappy 1/4 inch thick test piece).
- . transparency (fog density, Haze): emit resin molded 3 mm thick test piece, then according to ASTM D-1003 standard test transparency, when the Haze the higher the values of the represents transparency worse.
- . continuous phase (B) molecular weight 3, 000-50, 000 person content (weight %) measuring:

dissolving resin composition in tetrahydrofuran (referred to THF), through centrifugation removing does not dissolve composition, then dissolvable parts part by gel dialyzing method (referred to GPC) adopt polystyrene as standard measure its molecular weight distribution is; by the GPC measured range, molecular weight 3, 000-12, 000, 000 resin signal integration total area of serves as 100%, with a molecular weight 3, 000-50, 000's area accounts for integration total area of percentage. Above GPC includes the following conditions assay:

Tube pillar: KD-806M, detection device: RI-410, UV-486, mobile phase: THF(flow rate 1.0 c.c./min).

□. the content of polystyrene block (wt%) assay: taking out of rubber-like copolymer dissolved in benzene heating dissolves, then adding 1, 2-dichloro-third butyl hydroperoxide (1, 2-di-choro-t-butyl hydroperoxide) solution and osmium tetraoxide mixing is continued for heat 15 min, cooling and adding methanol and sulfuric acid shaking down, and then filtered with filter paper, dry dryness, weighed.

$$\text{聚苯乙烯嵌段含量 (wt\%)} = \frac{\text{过滤后的残渣净重}}{\text{橡胶共聚物重}} \times 100\%$$

wherein 聚苯乙烯嵌段含量-polystyrene block content; 过滤后的残渣净重-filtered residue weight ; 橡胶共聚物重-rubber copolymer weight

□. rubber and 1, 2-vinyl content (%) assay:

Measured by IR.

VIII. rubber particles therein occlusion structure content (%) photographs for determining: the resin to penetrate electron microscope shoot obtain 25000 times; fetching photograph 12 cm × 16 cm within the scope , measuring respectively the rubber particles total number of (N), and rubber particles coated with four or more than occlusion (occlusion diameter need of ≥ 0.05 μ) rubber particles number (N1), without occlusion to rubber particle number is (N2), that is to say, wherein rubber particle number N2 in contains: rubber particles within the totally without occlusion, or occlusion diameter of in 0.05 μm or 0.not more than 05 μm packet particles.

$N1 / N \times 100\% =$ or more than four encapsulated therein particles rubber particles content of%

$N2 / N \times 100\% =$ without occlusion rubber particles content of%

[Embodiments]

Embodiment 1 rubber-like copolymer 8.4 weight part (styrene/butadiene content =25 /75 weight %, 1, 2-vinyl content =15.4%, wood with Mooney viscosity as 45 progressive block polymerization article, the block polymerization contained in one with styrene block, one polybutadiene block, and one methyl benzene ethylene component gradual benzene ethylene/butadiene block, wherein polystyrene block content is 18 weight %), styrene 21.6 weight part, methyl methacrylate 34.5 weight part, acrylonitrile 5.5 weight parts, ethyl benzene 30 weight parts, dodecyl mercaptan 0.1 weight part, with peroxide benzoyl 0. 1 weight part to form the feed solution, the above-mentioned feed solution to 35kg/hr continuously pumping to four connected-in-series totally mixing type reactor (each kettle capacitance is 40 liter) continuous polymerization apparatus wherein first reactor reaction temperature is controlled at 110 °C, the second reactor reaction temperature is controlled at 115 °C, the third kettle reaction temperature is controlled at 125 °C, fourth kettle reaction temperature is controlled at 130 °C, and after reaction conversion rate about 57%, by removing volatile device extrusion, it can obtain the invention transparent rubber modified styrene resin.

Above composable continuous phase has styrene structure unit 32 weight part, methyl methacrylate 60 weight part, acrylonitrile 8 weight parts, molecular weight 3, 000-50, 000 person based on 29 weight %, rubber containing more than four occlusion structure particle number accounts for all the rubber 6%, without occlusion structure rubber particle number accounts for 64%, the resin determined physical property is shown as table 1.

Embodiment 2 rubber-like copolymer 8.4 weight part (styrene/butadiene content =25 /75 weight %, 1, 2-vinyl content =18.0%, wood with Mooney viscosity 47 progressive block copolymer), styrene 22.8 weight part, methyl methacrylate 37.0 weight part, acrylonitrile 1.8 weight parts, ethyl benzene 30 weight parts, dodecyl mercaptan 0.1 weight part, with peroxide benzoyl 0. 1 weight part to form the feed solution, the above-mentioned feed solution to 35kg/hr continuously pumping to four connected-in-series totally mixing type reactor (each kettle capacitance is 40 liter) continuous polymerization apparatus wherein a first kettle reaction temperature is controlled at 110 °C, the second reactor reaction temperature is controlled at 115 °C,

the third kettle reaction temperature is controlled at 125 °C, fourth kettle reaction temperature is controlled at 130 °C, and after reaction conversion rate about 60%, by removing volatile device extrusion, it can obtain the invention transparent rubber modified styrene resin.

Above composable continuous phase has styrene structure unit 34 weight part, methyl methacrylate 63 weight part, acrylonitrile 3 weight parts, molecular weight 3,000-50,000 person based on 34 weight %, and of rubber-like copolymer polystyrene block content is 19 weight %, rubber particles contain more than four occlusion structure person accounts for all the rubber particle number 8%, without occlusion structure rubber particle number accounts for 60%, the resin determined physical property is shown as table 1.

Embodiment 3 rubber-like copolymer 8.4 weight part (styrene/butadiene content =25 /75 weight %, 1, 2-vinyl content =15.4%, wood with Mooney viscosity as 45 progressive block copolymer), styrene 22.8 weight part, methyl methacrylate 37.0 weight part, acrylonitrile 1.8 weight parts, ethyl benzene 30 weight parts, dodecyl mercaptan 0.1 weight part, with peroxide dibenzoyl 0.1 weight part to form the feed solution, the above-mentioned feed solution to 35kg/hr continuously pumping to four connected-in-series totally mixing type reactor (each kettle capacitance is 40 liter) continuous polymerization apparatus wherein a first kettle reaction temperature is controlled at 110 °C, the second reactor reaction temperature is controlled at 115 °C, the third kettle reaction temperature is controlled at 125 °C, fourth kettle reaction temperature is controlled at 130 °C, and after reaction conversion rate about 60%, by removing volatile device extrusion, it can obtain the invention transparent rubber modified styrene resin.

Above composable continuous phase has styrene structure unit 34 weight part, methyl methacrylate 63 weight part, acrylonitrile 3 weight parts, molecular weight 3,000-50,000 person based on 33 weight %, and of rubber-like copolymer polystyrene block content is 18 weight %, rubber particles contain more than four occlusion structure person accounts for all the rubber particle number 5%, without occlusion structure rubbery particle number accounts for 65%, the resin determined physical property is shown as table 1.

Embodiment 4 rubber-like copolymer 8.4 weight part (styrene/butadiene content =25 /75 weight %, 1, 2-vinyl content =12.5%, wood with Mooney viscosity 49 progressive block

copolymer), styrene 22.8 weight part, methyl methacrylate 37.0 weight part, acrylonitrile 1.8 weight parts, ethyl benzene 30 weight parts, dodecyl mercaptan 0.1 weight part, with peroxide bibenzoyl 0.1 weight part to form the feed solution, the above-mentioned feed solution to 35kg/hr continuously pumping to four connected-in-series totally mixing type reactor (each kettle capacitance is 40 liter) continuous polymerization apparatus wherein a first kettle reaction temperature is controlled at 110 °C, the second reactor reaction temperature is controlled at 115 °C, the third kettle reaction temperature is controlled at 125 °C, fourth kettle reaction temperature is controlled at 130 °C, and after reaction conversion rate about 60%, by removing volatile device extrusion, it can obtain the invention transparent rubber modified styrene resin.

Above composable continuous phase has styrene structure unit 34 weight part, methyl methacrylate 63 weight part, acrylonitrile 3 weight parts, molecular weight 3, 000-50, 000 person based on 36 weight %, and of rubber-like copolymer polystyrene block content is 15 weight %, rubber particles contain more than four occlusion structure person accounts for all the rubber particle number 4%, without occlusion structure rubber particle number accounts for 58%, the resin determined physical property is shown as table 1.

Contrast example 1 rubber-like copolymer 8.4 weight part (styrene/butadiene content =30 /70 weight %, 1, 2-vinyl content =11.0%, wood with Mooney viscosity as 45 progressive block copolymer), styrene 24.6 weight part, methyl methacrylate 37.0 weight parts, ethyl benzene 30 weight parts, dodecyl mercaptan 0.07 weight part, with peroxide bibenzoyl 0.12 weight part to form the feed solution, the above-mentioned feed solution to 35kg/hr continuously pumping to four connected-in-series totally mixing type reactor (each kettle capacitance is 40 liter) continuous polymerization apparatus, but reaction temperature change to: a first kettle reaction temperature is controlled at 95 °C, the second reactor reaction temperature is controlled at 110 °C, the third kettle reaction temperature is controlled at 120 °C, fourth kettle reaction temperature is controlled at 125 °C, and after reaction conversion rate about 55%, by removing volatile device extrusion, it can obtain the invention transparent rubber modified styrene resin.

Above composable continuous phase has styrene structure unit 37 weight part, methyl methacrylate 63 weight part, its molecular weight 3, 000-50, 000 person based on 12 weight %, and of rubber-like copolymer polystyrene block content is 21 weight %, rubber particles contain

more than four occlusion structure person accounts for all the rubber particle number 1.8%, without occlusion structure rubber particle number accounts for 75%, the resin determined physical property is shown as table 1.

Contrast example 2 rubber-like copolymer 8.4 weight part (styrene/butadiene content =15 /85 weight %, 1, 2-vinyl content =15.4%, wood with Mooney viscosity as 45 progressive block copolymer), styrene 30.0 weight part, methyl methacrylate 28.0 weight part, acrylonitrile 3.6 weight parts, ethyl benzene 30 weight parts, dodecyl mercaptan 0.1 weight part, with peroxide benzoyl 0.1 weight part to form the feed solution, the above-mentioned feed solution to 35kg/hr continuously pumping to four connected-in-series totally mixing type reactor (each kettle capacitance is 40 liter) continuous polymerization apparatus wherein a first kettle reaction temperature is controlled at 110 °C, the second reactor reaction temperature is controlled at 115 °C, the third kettle reaction temperature is controlled at 125 °C, fourth kettle reaction temperature is controlled at 130 °C, and after reaction conversion rate about 58%, by removing volatile device extrusion, it can obtain the invention transparent rubber modified styrene resin.

Above composable continuous phase has styrene structure unit 47 weight part, methyl methacrylate 47 weight part, acrylonitrile 6 weight parts, molecular weight 3, 000-50, 000 person based on 33 weight %, and of rubber-like copolymer polystyrene block content is 2 weight %, rubber particles contain more than four occlusion structure person accounts for all the rubber particle number 9%, without occlusion structure rubber particle number accounts for 15%, the resin determined physical property is shown as table 1.

Contrast example 3 rubber-like copolymer 8.4 weight part (styrene/butadiene content =5 /95 weight %, 1, 2-vinyl content =18.0%, wood with Mooney viscosity as 45 progressive block copolymer), styrene 27.1 weight part, methyl methacrylate 32.7 weight part, acrylonitrile 1.8 weight parts, ethyl benzene 30 weight parts, dodecyl mercaptan 0.1 weight part, with peroxide benzoyl 0.1 weight part to form the feed solution, the above-mentioned feed solution to 35kg/hr continuously pumping to four connected-in-series totally mixing type reactor (each kettle capacitance is 40 liter) continuous polymerization apparatus wherein a first kettle reaction temperature is controlled at 110 °C, the second reactor reaction temperature is controlled at 115 °C,

the third kettle reaction temperature is controlled at 125 °C, fourth kettle for controlling reaction temperature 130 °C, and after reaction conversion rate about 61%, by removing volatile device extrusion, it can obtain the invention transparent rubber modified styrene resin.

Above composable continuous phase has styrene structure unit 44 weight parts, methyl methacrylate 53 weight part, acrylonitrile 3 weight parts, molecular weight 3, 000-50, 000 person based on 33 weight %, and of rubber-like copolymer polystyrene block content is 0%, rubber particles contain more than four occlusion structure person accounts for all the rubber particle number 30%, without occlusion structure rubber particle number accounts for 2%, the resin determined physical property is shown as table 1.

Contrast example 4 rubber-like copolymer 8.4 weight part (styrene/butadiene content =25 /75 weight %, 1, 2-vinyl content =15.4%, wood with Mooney viscosity as 45 progressive block copolymer), styrene 16.8 weight part, methyl methacrylate 43.0 weight part, acrylonitrile 1.8 weight parts, ethyl benzene 30 weight parts, dodecyl mercaptan 0.25 weight part, with peroxide bibenzoyl 0.14 weight part to form the feed solution, the above-mentioned feed solution to 35kg/hr continuously pumping to four connected-in-series totally mixing type reactor (each kettle capacitance is 40 liter) continuous polymerization apparatus, but reaction temperature change to: a first kettle reaction temperature is controlled at 120 °C, the second reactor reaction temperature is controlled at 125 °C, the third kettle reaction temperature is controlled at 130 °C, fourth kettle reaction temperature is controlled at 135 °C, after reaction conversion rate about 62%, by removing volatile device extrusion, it can obtain the invention transparent rubber modified styrene resin.

Above composable continuous phase has styrene structure unit 33 weight part, methyl methacrylate 64 weight part, acrylonitrile 3 weight parts, molecular weight 3, 000-50, 000 person based on 52 weight %, and of rubber-like copolymer polystyrene block content is 18 weight %, rubber particles contain more than four occlusion structure person accounts for all the rubber particle number 5%, without occlusion structure rubber particle number accounts for 65%, the resin determined physical property is shown as table 1.

Embodiment 5 rubber-like copolymer 9.0 weight part (styrene/butadiene content =25 /75 weight %, 1, 2-vinyl content =15.4%, wood with Mooney viscosity as 45 progressive block

polymerization article, wherein polystyrene block content is 18 weight %), styrene 24.2 weight part, methyl methacrylate 33.2 weight part, acrylonitrile 1.8 weight parts, N-phenyl maleinoyloxy imine 1.2 weight part, polydimethyl siloxanes 0.0045 weight parts, ethyl benzene 30.6 weight parts, dodecyl mercaptan 0.1 weight part, with di-peroxidation of third butyl-hexahydro-terephthalic acid esters 0.1 weight part to form the feed solution, the above-mentioned feed solution to 35kg/hr continuously pumping to four connected-in-series totally mixing type reactor (each kettle capacitance is 40 liter) continuous polymerization apparatus, and in addition, N-phenyl maleinoyloxy imine so as to 0.32kg/hr speed continuous is pumped into second reactor, wherein the first kettle reaction temperature is controlled at 100 °C, the second reactor reaction temperature is controlled at 105 °C, the third kettle reaction temperature is controlled at 115 °C, fourth kettle reaction temperature is controlled at 130 °C, and after reaction conversion rate about 60%, by removing volatile device extrusion, it can obtain the invention transparent rubber modified styrene resin.

Above composable continuous phase has styrene structure unit 28 weight part, methyl methacrylate 66 weight part, acrylonitrile 3 weight parts, N-phenyl maleinoyloxy imine 3 weight part, measuring its transparency (Haze) 6.1%, fluidity (g/10 min) 1.9, impact resistant intensity (kg/cm-cm) 18, chemistry pharmaceutical product resistance preferably (0). Composed of contrast example 1 experimental results learn that, when resin composition therein copolymer without acrylonitrile series monomer component, molecular weight 3, 000-50, 000's content of less than 15 weight %, superadd four or more occlusion structure rubber particle number slightly relatively low when , the resin processability of (fluidity) and chemistry pharmaceutical product resistance is not so good, simultaneously resin impact resistance is not perfect; from contrast example 2 test results learn that, when resin composition of rubber-like copolymer in polystyrene block content of less than 5 weight %, without containing occlusion structure rubber particle number ratio relatively low when , the resin transparency of the worse; when the polystyrene block of rubber-like copolymer content of less than 5 weight %, and has a four or more occlusion structure rubber particle proportion of the number of higher, without an occlusion structure rubber particle proportions in number relatively low when , the resin transparency in difference, the by contrast example 3 experimental results that can prove; in addition, composed of contrast example 4 learn that, when copolymer continuous phase molecular weight 3, 000-50, 000 user accounts for all

copolymer continuous phase (B) ratio higher than 50 wt% , impact resistance intensity and chemistry pharmaceutical product resistance worse. And Referring to various embodiments of the invention, the invention via control rubbery copolymer of in the content of polystyrene block, copolymer continuous phase (B) molecular weight 3, 000-50, 000 wearers' proportions, copolymer continuous phase (B) acrylonitrile series component, containing four or more occlusion structure rubber particle number ratio, and without an occlusion structure rubber particle proportions in number, truly can make resin composition has preferred chemistry pharmaceutical product resistance, processability, simultaneously also can obtain good transparency and impact resistance, thereby, the invention shows a novel, advances , and has the industry is utilizing value resin composition.

Table 1

Project \ Experiment No.		Embodiment				Contrast example			
		1	2	3	4	1	2	3	4
Continuous phase	Styrene monomer	32	34	34	34	37	47	44	33
	Methacrylate monomer	60	63	63	63	63	47	53	64
	Acrylonitrile monomer	8	3	3	3	—	6	3	3
	Molecular weight of 3,000 to 5,000 by the total weight%	29	34	33	36	12	33	33	52
Rubber copolymer	Styrene monomer content (wt%)	25	25	25	25	30	15	5	25
	Polystyrene content (weight%)	18	19	18	15	21	2	0	18
	1,2 - vinyl content (%)	15.4	18.0	15.4	12.5	11.0	15.4	18.0	15.4
Dispersive phase	Number of the rubber particle containing 4 or more occlusion structure by the total number of rubber particle%	6	8	5	4	1.8	9	30	5
	Number of the rubber particle without occlusion structure by the total number of rubber particle%	64	60	65	58	75	15	2	65
Physical	Flow properties (g/10 min)	2.0	2.1	2.3	2.5	1.3	2.0	1.8	5.0

property	Impact resistance (kg / cm-cm)	19	19	18	17	12	18	23	9
test	Transparency (haze)%	5.9	5.5	5.1	3.8	7.2	11.5	12.6	11
	Chemical resistance	○	○	○	○	×	○	○	△